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TECHNICAL REPORT # 5

INCORPORATION OF REACTIVE DYNAMICS IN SIMULATIONS OF CHEMICALLY SUSTAINED SHOCK WAVES*

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A two-dimensional molecular-dynamics model of a chemically-sustained shock wave in a molecular solid is discussed. A many-body expression that realistically describes chemical bonding in condensed phases is used for the interatomic potential. The results demonstrate that simple reactive collisions are sufficient to self-sustain a shock wave with a velocity that is comparable to experimental detonation velocities. Features characteristic of macroscopic detonations such as an intrinsic detonation velocity and a following flow are observed on a microscopic scale.

I. INTRODUCTION

Molecular dynamics (MD) simulation has proven to be an excellent method for studying atomic-scale reaction dynamics in a of variety systems. For this technique to be of use, however, the system to be studied should be restricted to atomic dimensions and short timescales (up to nanoseconds), and an adequate potential energy surface should be used. Nonreactive shocks provide ideal phenomena to be studied using MD techniques; the results of MD studies using Lennard-Jones potentials have compared very well to macroscopic models,[1] suggesting that shock waves in liquids and solids can be well described on an atomic scale. Detonating solids, however, require some form of energy release to self-sustain the shock wave, and so Lennard-Jones potentials are generally inadequate. Furthermore, to realistically model chemical energy release the forces should be many-body in nature since the reactivity of a given atom depends on its bonding to surrounding atoms. Analytic expressions that realistically describe changes in chemical bonding in the solid state have only recently been introduced, and with few exceptions[2] have been restricted to metals and semiconductors.[3]

In this work we present a two-dimensional microscopic model for a detonating molecular solid that is based on the many-body Tersoff covalent bonding formalism.[4] The simulations demonstrate that macroscopic features of detonating solids such as an intrinsic detonation velocity and a following flow are apparent on the microscopic level. The simulations display a detonation front that is on the order of a few atomic dimensions wide and a high density reaction region where much of the molecular nature of the solid is lost.

II. MODEL

Tersoff has recently introduced a simple analytic expression that realistically describes bonding in covalently-bonded solids.[4] Encouraged by this work (and additional extensions of this approach to few-body reactions[5]), we have adapted a simplified form of the Tersoff expression to model an energetic molecular solid. In this approach the binding energy is written in a form similar to a pair potential:

$$E_b = \sum_i \sum_{j(>i)} f_c(r_{ij}) \cdot [V_R(r_{ij}) - \overline{B}_{ij} \cdot V_B(r_{ij})$$

$$- (1 - \overline{B}_{ij}) \cdot V_{NB}(r_{ij})]. \tag{1}$$

The functions $V_R(r)$, $V_B(r)$ and $V_{NB}(r)$ represent repulsive, attractive bonding, and nonbonding pair-additive interactions, respectively, r_{ij} is the scalar distance between atoms i and j, and $f_c(r)$ is a function that restricts the range of the potential. The many-body aspect of the potential enters through $\overline{B}_{ij}$ which weakens the pair-additive bonding term (and hence the bond energy) between atoms i and j as the local coordination of the atoms increases. For our model it is also used to modulate the nonbonded interactions.

Following Tersoff, the function $\overline{B}_{ij}$ is given by

$$\overline{B}_{ij} = (B_{ij} + B_{ji})/2 \tag{2a}$$

where

$$B_{ij} = \{1 + G \sum_{k(\neq i,j)}{}' [\ldots \cdot exp(m \cdot (r_{ij} - r_{ik}))]\}^{-n}. \quad (2b)$$

Modified Morse functions of the form

$$V_R(r) = D_e/(S - 1)exp(-\beta\sqrt{2S}(r - r_e)) \quad (3)$$

and

$$V_A(r) = S \cdot D_e/(S - 1)exp(-\beta\sqrt{2/S}(r - r_e)) \quad (4)$$

are used for the repulsive and attractive bonding pair interactions, the nonbonded pair term is

$$V_{NB}(r) = r \cdot A_{NB}\, e^{(-B_{NB}\, r)}, \quad (5)$$

and $f_c(r)$ is

$$f_c(r) = \begin{cases} 1, & r < D_1 \\ \left[1 + cos\left(\frac{\pi(r - D_1)}{(D_2 - D_1)}\right)\right]/2, & D_1 < r < D_2 \\ 0, & r > D_2. \end{cases} \quad (6)$$

Eqs. 1–6, while maintaining the simplicity of a pair potential, incorporate general bonding concepts. In the limit of isolated diatomic molecules each $\overline{B}_{ij}$ equals one and Eq. 1 reduces to a sum of morse functions. As atomic coordination increases, the pair additive bond strengths decrease and the equilibrium distances increase in a way that yields the Pauling bond order relationship.[4] Since the functional forms are relatively simple, this approach is efficient for modeling the simultaneous reaction of many molecules, such as occurs in a condensed-phase detonation.

Rather than try to describe one particular system, we have developed a simple generic model for an energetic molecular solid. The parameters entering the function $\overline{B}_{ij}$ are chosen so that bonding pair terms are significantly weakened for atomic coordinations greater than one. This insures that the lowest-energy state of the system is a collection of diatomic molecules, and maintains the molecular nature of the solid at thermal temperatures and low pressures. They have also been chosen to reproduce chemically-sound potential barriers for reactive collisions. Energy release is incorporated by using two different kinds of atoms with different well depths in the morse functions (Eqs. 3 and 4). For heteronuclear diatomic molecules, a well of depth of 2 eV is used while for homonuclear diatomic molecules the well depth is 5 eV. The initial unreacted system is composed of heteronuclear diatomic molecules that are bound into a solid by weak nonbonded forces. After initiation, the chemically sustained shock is driven by the formation of the strong molecular bond in the homonuclear diatomic molecules. The atomic mass used in the simulations corresponds to nitrogen and the parameters used in Eqs. 1-6 are as follows: $\beta = 2.7 \text{Å}^{-1}$, $R_e = 1.0 \text{Å}$, $S = 1.8$, $G = 5.0$, $n = 0.5$, $m = 2.25 \text{Å}^{-1}$, $A_{NB} = 0.09 eV$, $B_{NB} = 0.67 \text{Å}^{-1}$, $D_1 = 3.0 \text{Å}$, $D_2 = 4.0 \text{Å}$.

III. RESULTS AND DISCUSSION

The shocks were initiated by striking a two-dimensional crystal with a simulated flyer plate that was composed of the same material as the initial crystal. Periodic boundaries were maintained in the direction perpendicular to the shock. Shown in Figs. 1a and 1b are snapshots from a simulation where the flyer plate was given an initial velocity of 5 km/sec. In Fig. 1a the initial shock can be identified by a distortion of the crystal structure. At about 10 Å behind the plate-induced shock front some of the molecules have collided and begun reacting. Fig. 1b shows the system after ≈ 8 ps. At this point the initial shock caused by the flyer plate has diminished, while the chemically-sustained shock continues to propagate. A hot gas consisting mostly of product molecules and a few free atoms and reactant molecules is visible expanding out the back of the shock at the left of Figs. 1a and 1b, and a high density region separating the gas from the shock front is visible in the center of Fig. 1b.

The velocities of the front edge of chemically-sustained shocks versus time are given in Fig. 2 for two different simulations. The dotted line is from the simulation described above and the solid line is from a simulation that used an impact plate velocity of 10 km/sec. In the latter case the chemical reactions began at the plate-solid interface, with no leading plate-induced shock wave. After a brief period both of the chemically-driven shocks reach the same constant velocity of 4.8 km/sec. The steady-state velocity of the chemically-sustained shock is apparently an intrinsic property of the microscopic system.

Despite the microscopic size of the system simulated here, the model displays behavior characteristic of macroscopic detonations. First, for the 5 km/sec impact plate velocity a nonreactive compressional wave preceeds the detonation front. This is similar to real systems where detonation is initiated behind a leading shock wave.[6] Second, the detonation velocity predicted by our simple model agrees very well with experimental velocities (typically 3-7 km/sec). It should be emphasized that no adjustment of the potential was made to achieve this
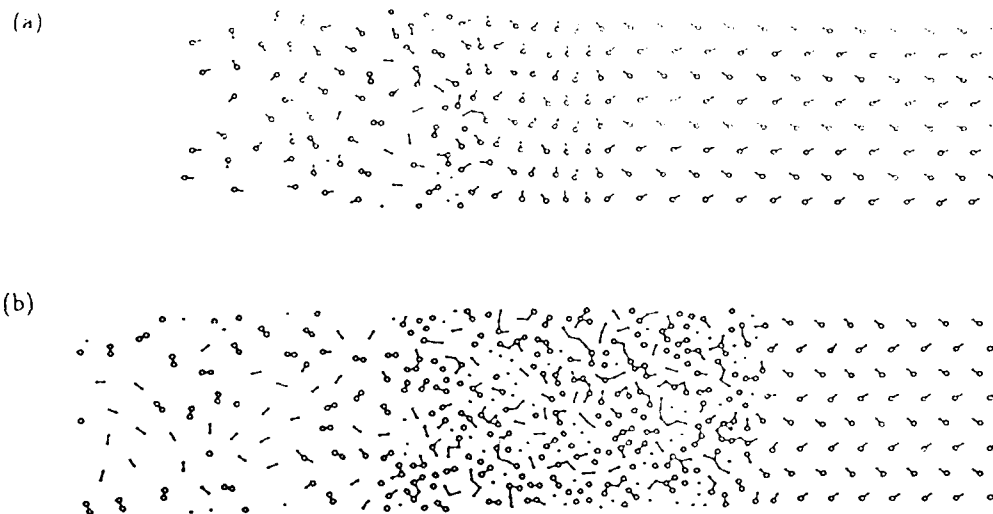
FIG 1. Snapshots from the simulation. The two types of atoms are drawn with different sizes, and lines connect atoms that are within 1.4 Å. The shock is traveling from left to right. a) The system from -20 Å to 100 Å at 1 ps. b) The system from 280 Å to 300 Å at 8 ps.

velocity, rather it is a prediction of the model. Furthermore, this velocity is intrinsic to the material, again in agreement with macroscopic systems. Third, the high-density region (apparent in the center of Fig. 1b) exhibits a steady forward flow of ≈4.2 km/sec, and its width increases linearly. For long times this region would presumably evolve into a macroscopic following flow, in agreement with continuum models.[7]
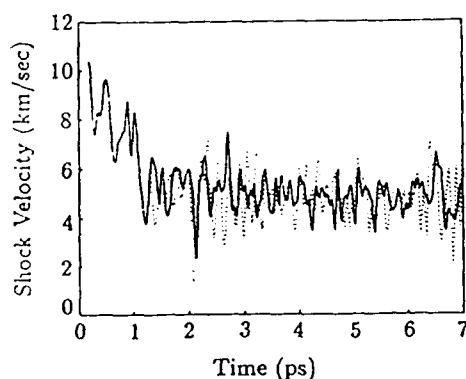
The atomic-scale structure and dynamics of the chemically-sustained shock is of particular interest, since this regime in a real detonation is not easily accessible to experiment. Shown in Fig. 3 is the potential energy per particle versus position (relative to the shock front) calculated from the simulation. The unreacted material is to the right of the figure and the shock front is at zero.

FIG. 2 Velocities for chemically-sustained shock fronts versus time.
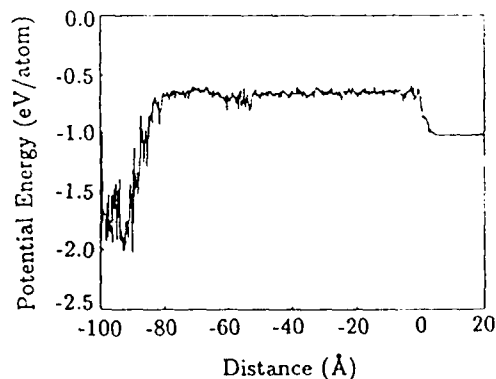
Fig. 3. Potential energy versus position relative to the front. The front is at 0 Å and unreacted material is to the right. Expansion into the gas phase begins at ≈80 Å behind the front.

The figure represents an average over 25 configurations at 5.8 ps into the simulation. At the shock front the potential energy rises sharply to a value that remains constant throughout the high density region, and the potential energy does not drop to a value lower than the unreacted material until the molecules expand into the gas phase. Apparently chemical energy is not fully accessed until the gas-phase molecules are formed. This picture of the potential energy corresponds well with Fig. 1b; although distinct molecular units are apparent as reactant and product molecules, in the high-density region the molecules are undergoing multiple collisions and the molecular nature of the solid is lost.

Several extensions to the model are possible. First, only one choice of parameters for the potential energy expression has been discussed. The functional form is sufficiently flexible that features of the potential energy surface can be changed so that relationships between reaction kinetics and detonation[8] can be studied. Second, the microscopic characteristics of the simulation may be influenced by the reduced dimensionality of the simulations. Because the form of the potential is not restricted to low dimensions, extension of our model to three-dimensions is straight forward. Third, although changes in bonding are realistically described by the model, the system presented here is simple compared to real energetic materials. More complicated forms of the potential energy expression given above have been used to decribe condensed-phase carbon[9] and the exchange reactions $H+H_2$ and $O+O_2$,[5] and so the further development of our model to describe real systems appears promising. Finally, no attempt has been made to include effects outside of simple nuclear collisions. Although such effects may ultimately prove important, the results presented here suggest that simple collisional models are a good starting point for describing many of the properties of detonating solids.

ACKNOWLEDGMENTS

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